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Novel method for chemical vapor deposition and atomic layer epitaxy using radical chemistry

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Novel method for chemical vapor deposition and atomic layer epitaxy using radical chemistry

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Abstract

A novel method for chemical vapor deposition and atomic layer epitaxy using radical precursors under high vacuum conditions is being developed. The combination of selectively-generated radicals and high vacuum is ideal for low-temperature growth: growth rates remain relatively high because activation energies for radical reactions are typically small, and contamination and segregation are minimized by keeping the surface "capped" by adsorbed intermediates and working under ultraclean conditions. Fluorine atoms are generated by thermal dissociation in a hot tube and abstract hydrogen atoms from precursor molecules injected immediately downstream of the source, generating radicals with complete chemical specificity. Preliminary results on growth of diamond films using the new method are presented.

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I. INTRODUCTION

Atomic layer epitaxy (ALE) is a powerful technique for growing semiconductor materials one atomic layer at a time [1]. Relative to more conventional growth methods, ALE possesses several distinct advantages, which are likely to be critical to development of the next generation of electronic devices: (*i*) the *digital* nature of the process, i.e., growth of a well-defined number of monolayers, offering the ultimate in control of film thickness; (ii) the *uniformity* of growth on large-area substrates, since each reaction cycle runs to completion regardless of deviations in reactant fluxes; (iii) intrinsic capability for *atomically abrupt* heteroepitaxial interfaces. In addition, ALE processes are normally carried out at lower temperatures than the corresponding CVD process, again allowing smaller and more sharply defined circuit elements to be fabricated.

Originally proposed for growth of II-VI materials, ALE has been widely applied to growth of GaAs and other III-V semiconductors [1]. However, ALE is still in its infancy for Group IV semiconductors. Nishizawa *et al.* [2] demonstrated ALE with a growth rate of one monolayer per cycle using alternating fluxes of SiH_2Cl_2 and H_2 at a reported temperature of 825°C, while Lubben *et al.* [3] obtained a growth rate of 0.4 monolayers per cycle from a cycle involving alternating Si_2H_6 doses and UV laser pulses at substrate temperatures of 180 - 400 °C. Preliminary accounts of ALE on germanium [4] and diamond [5] as well as on silicon [6] have also been reported.

Radical chemistry would be ideal for ALE but has not yet been applied to any ALE process. Dichlorosilane is not highly reactive, thus necessitating high growth temperatures [2]. Disilane is more reactive than dichlorosilane but not as reactive as radicals, and adsorption saturates at coverages considerably below one monolayer [3]. The attainment of low growth temperatures is a central goal of current research--interdiffusion is greatly reduced, which is essential in fabricating circuit elements smaller than 0.1 micron, and the effects of differential thermal expansion coefficients in complex layered materials are minimized. However, the use of low temperatures introduces stringent demands on the cleanliness of the process. A process that involves creating a clean surface for adsorption, e.g., of Si_2H_6, will be very susceptible to contamination, and segregation, interdiffusion, and three-dimensional island formation in Ge_xSi_{1-x} heterstructures all occur more readily on clean than on covered surfaces [7,8]. While there is evidence that Si_2H_6 can react with hydrogenated silicon surfaces at substrate temperatures above 400 °C [9-11], growth at these temperatures appears not to be self-terminating. An ideal ALE growth process would take place at low temperature and keep the surface covered by protective groups during the process so as to minimize contamination and segregation. *Radical* reactants can create their own surface "site" by abstracting adsorbed atoms which stabilize and protect the substrate lattice from less reactive species (e.g., contaminants). Radicals thus are conducive to low-temperature growth, as creation of vacant sites by thermal desorption is not necessary, and simultaneously provide an elegant solution to the contamination and segregation problem, viz., capped surfaces. Another advantage of radical precursors is that once adsorbed, radicals are much more likely to decompose (yielding growth) than to simply

desorb (yielding nothing). This preference for decomposition over desorption is the most likely explanation for why CH_3 is a more effective growth precursor for diamond than C_2H_2 [12-15].

Performing growth from radical precursors in a high vacuum environment offers several additional advantages. Gas-phase collisions subsequent to radical formation can be kept to a minimum, enabling the creation of very specific radicals. Two mechanistic advantages are that the identity of the reactant species responsible for growth is easy to determine, and surface analytical techniques can be more readily applied in order to understand the surface chemistry. Control of contamination is facilitated by an ultraclean, UHV-compatible environment. Finally, in a high vacuum environment ALE reaction cycle times associated with switching gases can in principle be reduced to the millisecond time scale, allowing for substantial growth rates, which is very important if group IV ALE is to become a commercially significant process.

As a general growth technique, remote plasma enhanced CVD (RPCVD) [16,17] comes close to the ideal, as it generates reactive species without allowing the plasma to damage the sample by direct contact. However, RPCVD does *not* selectively produce reactive radicals--interaction of excited atoms, ions and electrons with the molecular growth precursor (e.g., SiH_4) can generate a variety of reactive species, which may produce defects. For ALE, a more serious problem is that *two* reactive species are produced from each molecular precursor, e.g., SiH_3 + H, which complicates and may prevent growth reactions from being self-limiting and reduces the flexibility of the process. Better would be a process where *well-defined radical species are produced without side reactions.*

We are developing a new ALE method for epitaxial growth of diamond, silicon, and germanium, using gas phase radicals under high vacuum conditions (effective pressure above the substrate: up to 0.1 Torr, background pressure < 10^{-2} Torr). Considerations affecting the choice of radical precursors and the apparatus and radical generation scheme are described in the next two sections. Preliminary results on radical generation and film growth of diamond are presented next, followed by a discussion.

II. RADICAL GROWTH CHEMISTRY

For ALE, the radical growth precursor should not be *too* reactive, or else the reaction will not be self-terminating. In the context of diamond or silicon ALE, for example, carbenes and silylenes (CX_2 or SiX_2, X= H, F, Cl, etc.) are too reactive to be useful. These species will readily insert into C-H or Si-H bonds, producing CX_2H or SiX_2H, which in turn can undergo another insertion reaction. In addition, a less reactive radical will yield better *selectivity*, e.g., the rate of reaction with tertiary hydrogen atoms will be much greater than the rate with secondary hydrogen atoms.

Monovalent radicals would seem to be ideal for sticking to dangling bonds on group IV semiconductor surface. What types of radicals are well suited for ALE processes? Consider the

growth step in a general, ALE-type radical-surface growth process, where A = C, Si, or Ge, and X and Y represent arbitrary functional groups:

$$\text{A-Y(s)} + {}^{\bullet}\text{AX}_3\text{(g)} \longrightarrow \text{A-}^{\bullet}\text{(s)} + \text{AYX}_3\text{(g)} \quad (1)$$

$$\text{A-}^{\bullet}\text{(s)} + {}^{\bullet}\text{AX}_3\text{(g)} \longrightarrow \text{A-AX}_3\text{(s)} \quad (2)$$

A surface Y group is abstracted by an AX_3 radical; a second AX_3 radical then adsorbs on the resulting dangling bond site. For reactions (1) and (2) to be self-terminating, the reaction of $AX_3(g)$ with A-Y(s) must be much faster than the reaction with A-X(s):

$$\text{A-AX}_3\text{(s)} + {}^{\bullet}\text{AX}_3\text{(g)} \longrightarrow \text{no reaction} \quad (3)$$

Abstraction of hydrogen atoms is much more facile than abstraction of halogen atoms, for both alkyl [18] and silyl radicals [19]. Thus, the most natural choice is Y=H, X=halogen. As an example, alternating cycles of CCl_3 and H are likely to be a good choice for ALE of diamond, as self-termination should occur naturally. The reaction of CCl_3 with a hydrogenated diamond surface will self-terminate because the activation energy for abstraction of H by CCl_3 is lower by at least 15 kcal/mol than the activation energy for abstraction of Cl [18]. In contrast, the activation energies for abstraction of Cl and primary hydrogen by CH_3 are nearly the same [18], so that the reaction of methyl radicals with a chlorinated diamond surface is unlikely to self-terminate and cycles of CH_3 and Cl are a *poor* choice for diamond ALE.

To complete the ALE cycle, a hydrogenated surface can be regenerated from the halogen-terminated surface (produced by adsorption of AX_3) by abstraction and recombination reactions with atomic hydrogen:

$$\text{A-AX}_x\text{(s)} + \text{H (g)} \longrightarrow \text{A-H}_x + \text{HX (g)} \quad (4)$$

where uncertainty in the actual stoichiometry in the surface species is indicated by the x subscript (= 1, 2, or 3) and stoichiometric coefficients are omitted from the equation. We have opted to use hydrogen atoms because H abstracts halogen atoms from carbon much better than do carbon-centered radicals [18]. Recent work by Yates and co-workers has shown that abstraction of Cl, Br, and I from Si(100) by atomic hydrogen is quite facile, with activation energies ≤ 2 kcal/mol [20]. On silicon, SiH_3 is also an excellent halogen abstractor, and alternating cycles of $SiCl_3$ and SiH_3 might yield a good ALE process.

In summary, then, in our proposed ALE sequence a trihalo radical (AX_3) reacts with a hydrogenated surface ($A\text{-}H_x$), first by abstraction of surface hydrogen and then recombination with the vacant site, to yield a halogenated substrate which has been augmented by one monolayer (or perhaps a fraction of a monolayer). Atomic hydrogen is then allowed to react with the halogenated surface, regenerating a hydrogenated surface. This scheme is illustrated schematically in Fig. 1.

The uncertainty in the stoichiometry of the self-terminated surface adlayer ($A\text{-}AX_x$) in Eq. (4) reflects an uncertainty in the saturation coverage of this species and, consequently, in the number of

monolayers per cycle that would result from this sequence. Neglected in Eq. (2) is the fact that steric repulsion will prevent formation of a complete monolayer of A-AX_3. Formation of a full (1×1):2H dihydride surface (i.e., AH_2), on Si(100) has until recently been controversial [21] (observation of a (1×1) diffraction pattern does not prove that a full dihydride has formed), and on diamond (100) the dihydride appears to be too sterically hindered to form under growth conditions [22,23]. Given the much larger covalent radius for Cl than H, it seems clear that a full monolayer of ACl_2 groups will not fit on either diamond or silicon, and the saturation coverage of ACl_3 would be even smaller.

Two possible resolutions of the saturation coverage question are envisaged. The first is that under growth conditions, the adsorbed AX_3 groups will probably not remain intact. For example, SiH_3 groups on Si(100) decompose to SiH_2 + H [24,25] at temperatures between 200 and 600 K, depending on the surface hydrogen coverage [25]. A second possibility is that some of the surface halogen atoms will react with surface hydrogen and desorb as HX, and the relatively favorable kinetics of dehydrohalogenation reactions served as an additional motivation for choosing halogen/hydrogen chemistry for the ALE growth chemistry. Reaction of X atoms might take place with preadsorbed hydrogen left over from the last hydrogenating cycle, or alternatively could be present in the precursor (AHX_2 rather than AX_3).

III. EXPERIMENTAL

Our radical CVD/ALE reactor, which has conceptual similarities to a remote-plasma-enhanced CVD reactor but uses thermally dissociated fluorine instead of discharge-excited He or Ar and has a UHV-compatible, corrosive-service turbomolecular pump which can handle a heavy load of corrosive gases, is illustrated schematically in Fig. 2. The turbomolecular pump is backed by an integral molecular drag stage and by an oil-free diaphragm pump. F_2 or XeF_2 is injected into a MgO tube heated to a temperature of 700-800 °C, yielding fluorine dissociation in the range of 96-98% at a pressure of ≈1 Torr [26]. Undissociated F_2 should be able to react with the radicals produced by H abstraction [27]. MgO is chosen as the wall material because MgF_2, which will form on the inside wall of the tube, is among the least volatile of all the fluorides, with a vapor pressure of 10^{-8} to 10^{-6} Torr in this temperature range. The principal advantages of a thermal source relative to a discharge source are simplicity, low cost, and flexibility in the choice of gas pressures and flow rates (maintenance of a plasma discharge requires a substantial pressure and flow rate). For a scaled-up reactor, a plasma F-atom source would probably be preferable. The fluorine atoms abstract hydrogen atoms quantitatively from precursor molecules injected in excess downstream from the F source where the gas density is high enough for collisions. The extreme reactivity of fluorine atoms toward hydrogen drives the reaction to completion, producing HF (135 kcal/mol bond energy), which is nonreactive to hydrogen-terminated diamond, silicon, and germanium in the absence of water. The radicals (and HF) formed downstream of the F-atom source flow under

nearly collision-free conditions to the substrate. F-atom-based secondary generation of radicals has been used to perform etching of semiconductor substrates (at rates up to 1000 Å/min) [27] but is being applied to growth for the first time in the present work.

The gas handling system is constructed of stainless steel tubing and fittings, with most of the joints made with VCR fittings. The flow rates of reactant gases are controlled with piezoelectric valves, which have rapid switching times and hence will be well suited to ALE, and are monitored by mass flow meters.

Our initial film growth efforts have focused on diamond. Since no one has successfully demonstrated diamond film growth at pressures less than ≈1 Torr to date, to the best of our knowledge, we felt it essential to demonstrate growth by CVD (continuous reactant fluxes) before attempting ALE. Preliminary results have been obtained using mixtures of H_2 and $CHCl_3$ and of H_2 and CH_4 as precursor gases. Typical flow rates were 0.75-1.5 sccm of F_2, 5-6 sccm of H_2, and 1-2 sccm of CH_4 or 4-6 sccm of $CHCl_3$. The chamber pressure rose to ≈ 10^{-2} Torr during growth.

The substrates were type 2A, (100)-oriented natural diamond windows, $3.0 \times 3.0 \times 0.22$ mm^3 in dimension, purchased from Dubbeldee Harris. Two different substrate holding/heating schemes have been employed. The first used 0.025-mm-thick Pt foil, heated resistively, as both holder and heater. The sample temperature was measured by a chromel-alumel thermocouple spot-welded to the foil immediately adjacent to the sample. The second sample holder consisted of two graphite rods, 1.6 mm in diameter, with the sample held between them in slots machined in the sides of the rods. The thermocouple was embedded in one of the graphite rods. The latter scheme has the advantage of providing a rigid sample support, which is very helpful for thickness measurements. The samples were held at 850-950 °C during the growth experiments.

Films were characterized by Raman spectroscopy and scanning electron microscopy. Film thicknesses were determined by measuring the total thickness of the diamond (100) substrates before and after growth from the fringe pattern in Fourier transform infrared transmission spectra [13(b)].

IV. RESULTS

Our initial tests of the radical source focused on demonstration of radical production. Mass spectra of $CHCl_3$ and of CCl_3 produced by hydrogen abstraction by atomic fluorine are shown in Fig. 3. Mass spectrometry of chlorohydrocarbons are complicated by the existence of both 35 and 37 amu isotopes of chlorine and by electron-impact-induced loss of H. The latter can be eliminated by reducing the electron energy in the ionizer to just above the ionization threshold. The spectra shown in Fig. 3 were obtained at an electron energy of 15.9 eV, which was found to be sufficiently low to suppress the H-loss mass peaks. The mass spectrum of $CHCl_3$ injected alone (Fig. 3(a)) shows prominent peaks at m/e = 118, 120, and 122, with a minor peak at 124 amu, corresponding to the parent ions. The observed intensity ratios correspond well to that expected from the ≈ 3:1

^{35}Cl-to-^{37}Cl natural isotopic abundance ratio. After heating the MgO tube furnace to 760 °C and injecting F_2 into it, the mass spectrum shown in Fig. 3(b) was obtained. Small peaks at m/e = 117, 119, and 121 amu are visible, corresponding to CCl_3 radicals. The low signal-to-noise ratio is the result of the low electron energy, together with the fact that a single stage of differential pumping is insufficient to properly discriminate against background gases–considerable recombination of the CCl_3 radicals takes place within both the reactor and the mass spectrometer chamber. Nonetheless, the difference between the two mass spectra gives a clear indication of radical formation.

To date the best evidence we have obtained for diamond growth using the new method is a film grown using $CHCl_3$ as the precursor which increased in thickness by 1.4 μm in 12 hours, corresponding to a modest growth rate of 0.12 μm/hr. We conservatively estimate the uncertainty in the thickness measurements to be ±0.5 μm, so the thickness increase appears to be real. A scanning electron micrograph of this film is shown in Fig. 4, and a Raman spectrum obtained after growth is shown in Fig. 5. The SEM image also suggests that growth has occurred: the linear features arranged by 90° with respect to one another on the left-hand portion of the image are highly suggestive of ledge features arising from growth, as the (100) substrate has square symmetry, steps and/or ledges along $[01\bar{1}]$ and $[0\bar{1}1]$ are commonly observed in [100]-oriented epitaxy, the as-polished substrate had no such features originally, and etching under high vacuum conditions normally roughens surfaces rather than creating regular features. Deposits of metal fluorides (NiF_2, TaF_5, but not MgF_2) were observed on portions of the sample holder and on the chamber walls, and could be responsible for the globular features on the right-hand portion of Fig. 4. Surface contamination may have reduced the growth rate. The radical source and sample holder have since been modified to reduce or eliminate reaction of F_2 with the hot surfaces in the reactor. The Raman spectrum indicates that no non-diamond carbon was deposited, to within our sensitivity limit, as no feature near 1550 cm^{-1} associated with graphitic carbon is visible.

IV. DISCUSSION

We have proposed a new method for atomic layer epitaxy and chemical vapor deposition, using radical precursors under high vacuum conditions. We have presented a rationale for the use of cycles of halogenated radicals and atomic hydrogen for growth of the group IV semiconductors diamond, silicon, and germanium based on well-known radical chemistry, and have delineated some of the issues involved in determining the number of monolayers per cycle that can be deposited using this chemistry.

We have chosen to generate the radicals with a secondary source using thermally-dissociated fluorine atoms. This approach has several advantages: well-defined radical species may be produced without side reactions; a very wide variety of radicals may be produced using standard, commercially-available precursor gases; the reactor and process can be readily scaled up without inordinate effort or cost; the basic methodology should be applicable to synthesis of a wide variety

of materials; and the complexity, cost, and power-consumption of discharge sources are avoided. The principal drawback of the F-atom-abstraction approach is the production of HF. The HF abstraction product necessitates the use of corrosion-resistant pumps and will prevent the growth of materials which are strongly attacked by HF, even in the absence of water. For example, in order to grow silicon by this method it will almost certainly be necessary to work at substrate temperatures low enough that the surface hydrogen (or halogen) coverage remains very high throughout the process so as to passivate the surface to HF adsorption. HF adsorbs readily on *clean* Si(100) [28], and the dominant pathway for surface fluorine removal is likely to be desorption of SiF_2, i.e., etching, although abstraction by atomic hydrogen is also a less deleterious possibility. A disadvantage of the thermal dissociation source relative to a discharge source is that materials compatibility issues are more stringent. We find, for example, that if a significant fraction of the F_2 is not consumed by abstraction and the Ni foil has not been carefully passivated, the Ni foil becomes etched and fails within several days.

Further diamond growth experiments are currently underway in our laboratory. We hope to improve several aspects of the experiments, including the reliability of the radical source and the sensitivity of the growth rate measurements. Once incontrovertible evidence for diamond growth has been achieved, we hope to be able to achieve ALE by cycling the reactant fluxes.

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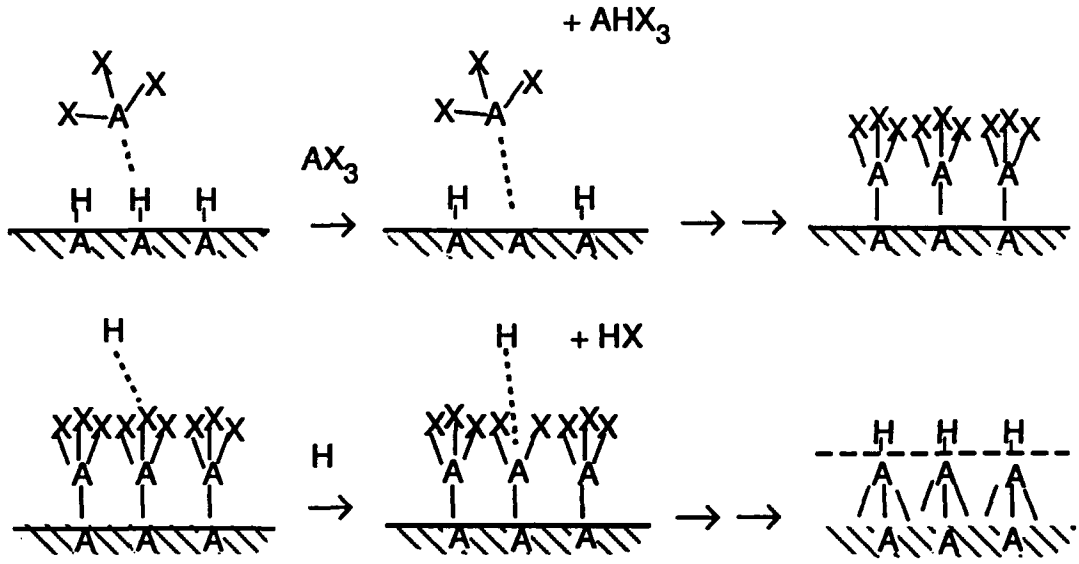

Fig. 1. Schematic representation of radical ALE growth chemistry. In the first, "growth" portion of the ALE cycle, tri- (or di-) halo-radicals (A = C or Si) impinge on a hydrogen-terminated surface, abstracting hydrogen atoms and creating vacant surface sites. Radicals then quickly adsorb on the vacant site. When the surface becomes halogen-terminated the reaction stops, since abstraction rates of halogen atoms are much lower than of hydrogen atoms. In the "cleaning" or "reactivation" cycle, hydrogen atoms abstract surface halogen atoms and then stick to the vacant surface sites, regenerating the hydrogen-terminated surface which has been augmented by one monolayer. This illustration is oversimplified, as a full monolayer of trihalide species will not fit on either Si(100) or diamond (100) surfaces–either rearrangements or else desorption of HX must take place.

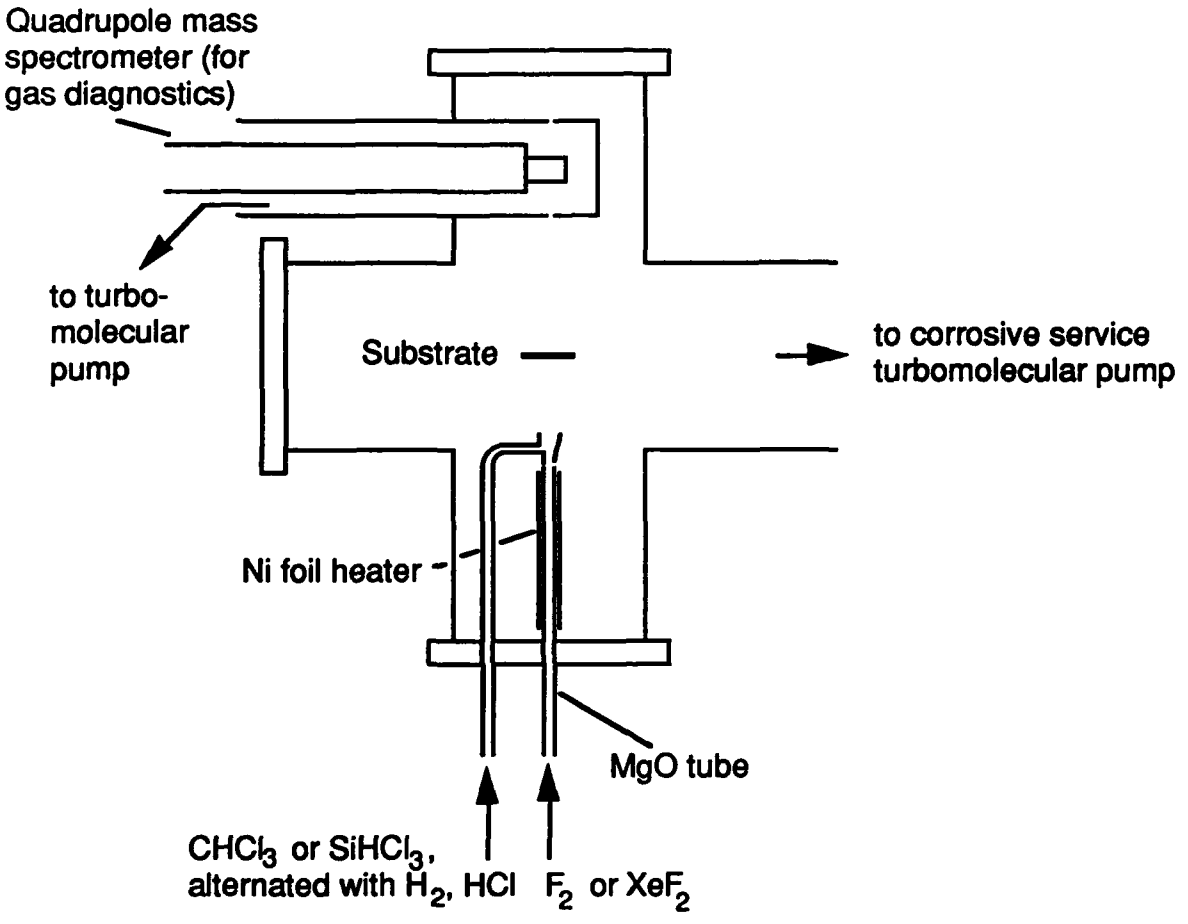

Fig. 2. Schematic of ultrahigh-vacuum-compatible radical ALE growth apparatus. Precursor molecules are injected into a stream of fluorine atoms generated by thermal dissociation in a MgO tube heated by Ni foil, producing radicals + HF. The radicals are then transported to the substrate, essentially without further collisions.

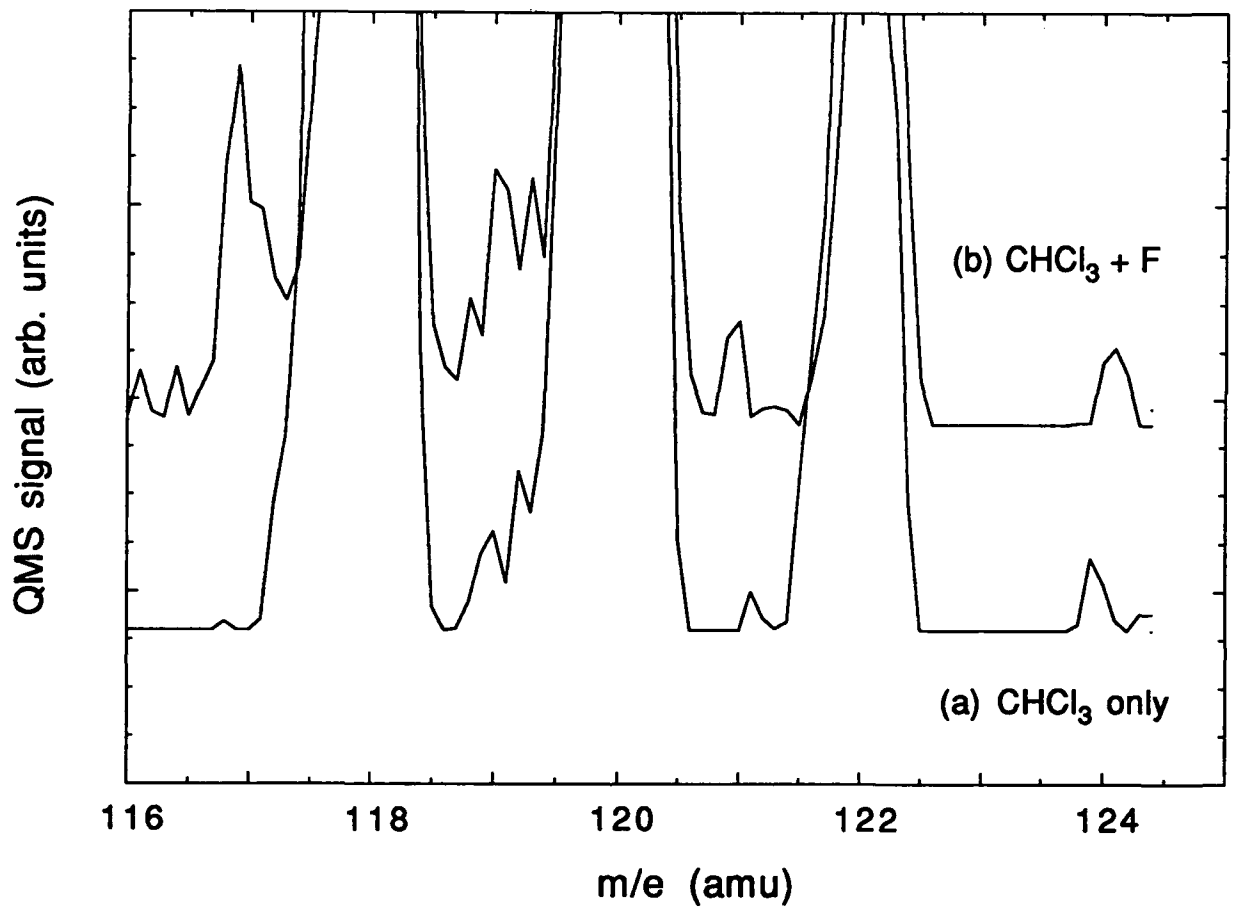

Fig. 3. Threshold ionization mass spectra of (a) $CHCl_3$ only and (b) $CHCl_3$ injected into a stream of F atoms. The mass spectra were obtained at an electron energy of 15.9 eV.

Fig. 4. Scanning electron micrograph of film grown on a diamond (100) substrate.

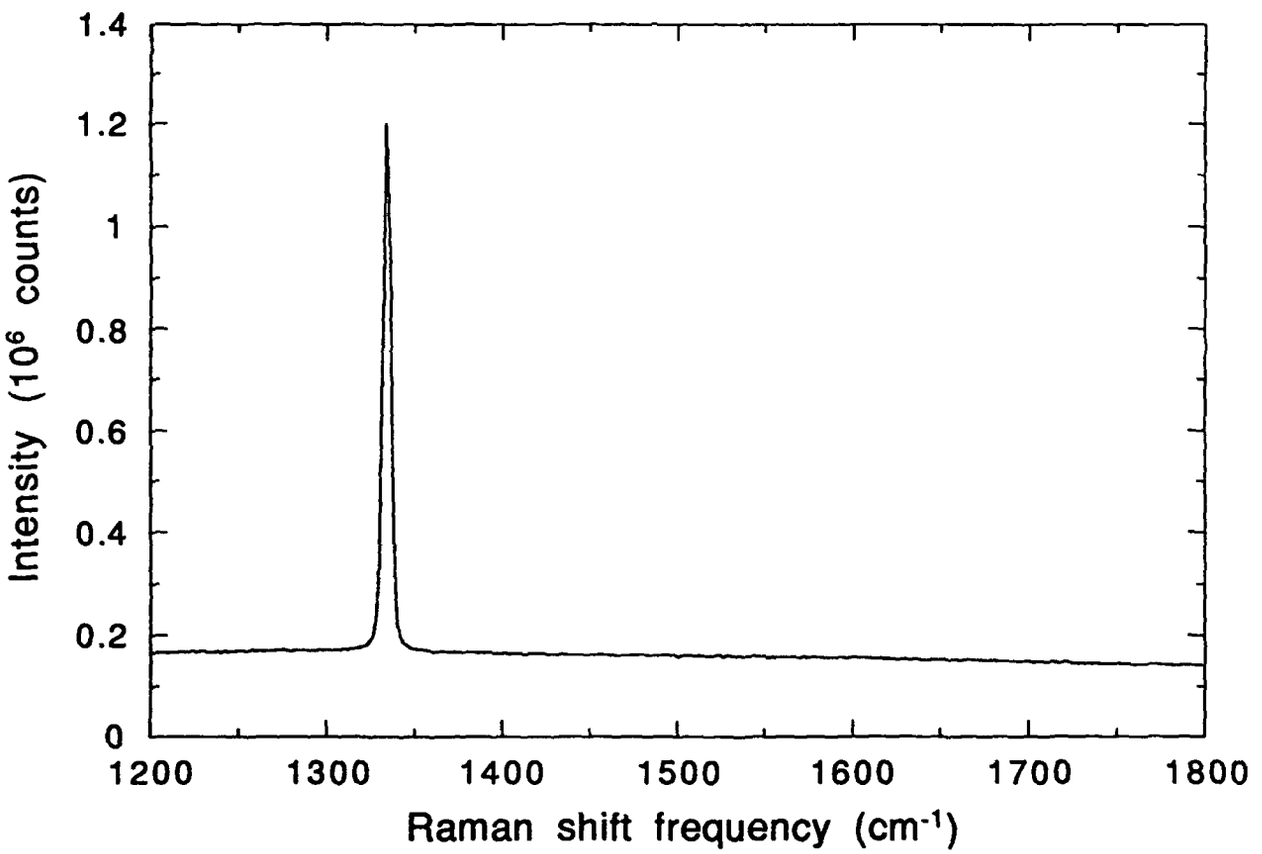

Fig. 5. Raman spectrum of film grown on a diamond (100) substrate.